

Supporting Information

For

The Nature of the Mn(III) Color Centers in Elbaite Tourmalines

Daniel A. Kurtz¹, George R. Rossman^{2,}, Bryan M. Hunter^{1,3,*}*

¹Rowland Institute at Harvard University, Cambridge, MA, USA

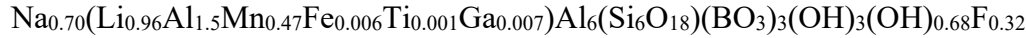
²Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, USA

³Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA

Corresponding author email addresses: bhunter@rowland.harvard.edu, grr@gps.caltech.edu

Determination of Mn concentration in sample

From EMP data, empirical formula is



$$\text{Mn}\% \text{ in } Y \text{ site} = \frac{0.47}{2.945} * 100\% = 16.0\% \text{ Mn ions} \quad (1)$$

There are 7.5 Y site ions in a single unit cell, therefore:

$$\# \text{Mn in unit cell} = 7.5 \text{ ions} * 16.0\% \text{ Mn ions} = 1.20 \text{ Mn ions/unit cell} \quad (2)$$

$$1.20 \text{ Mn ions/unit cell} * \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ ions}} = 1.99 \times 10^{-24} \text{ mol Mn ions/unit cell} \quad (3)$$

According to crystal structure data from reference 1, unit cell volume is $1,530 \text{ \AA}^3$, or $1.53 \times 10^{-24} \text{ L}$.

$$\text{Conc of Mn ions} = \frac{2.18 \times 10^{-24} \text{ mol Mn ion}}{1.53 \times 10^{-24} \text{ L}} = 1.30 \text{ M Mn ions} \quad (4)$$

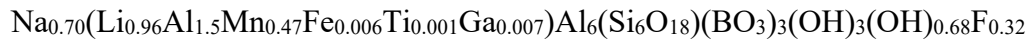
Determination of the extinction coefficient of the transition ${}^5\text{E}(\text{a}_1)^1(\text{e})^2(\text{e})^1 \rightarrow {}^5\text{E}(\text{a}_1)^1(\text{e}_2)^1(\text{e}_2)^2$ at 530 nm (1.81 AU, E1c)

Assuming that all Mn is converted to Mn^{3+} upon irradiation with a dose of 240 Mrad, then:

$$\varepsilon = \frac{\text{Abs}}{l * \text{conc}} = \frac{1.81}{(0.565 \text{ cm}) * (1.30 \text{ M})} = 2.47 \text{ M}^{-1} \text{cm}^{-1} \quad (5)$$

Determination of Fe concentration in sample

From XRF data, empirical formula is



$$\text{Fe}\% \text{ in } Y \text{ site} = \frac{0.006}{2.954} * 100\% = 0.20\% \text{ Fe ions} \quad (6)$$

There are 7.5 Y site ions in a single unit cell, therefore:

$$\# \text{Fe in unit cell} = 7.5 \text{ ions} * 0.20\% \text{ Fe ions} = 0.015 \text{ Fe ions/unit cell} \quad (7)$$

$$0.015 \text{ Fe ions/unit cell} * \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ ions}} = 2.5 \times 10^{-26} \text{ mol Fe ions/unit cell} \quad (8)$$

According to crystal structure data from reference 1, unit cell volume is $1,530 \text{ \AA}^3$, or $1.53 \times 10^{-24} \text{ L}$.

$$\text{Conc of Fe ions} = \frac{2.5 \times 10^{-26} \text{ mol Fe ion}}{1.53 \times 10^{-24} \text{ L}} = 0.017 \text{ M Fe ions} \quad (9)$$

Determination of the extinction coefficient of transition at 700 nm (0.079 AU, Fe(II) *d-d*, 0.079 AU, E_{||}c)

$$\varepsilon = \frac{Abs}{l*conc} = \frac{0.048}{(0.565\text{ cm})*(0.017\text{ M})} = 5.1\text{ M}^{-1}\text{cm}^{-1} \quad (10)$$

Determination of the extinction coefficient of transition at 1,030 nm (0.079 AU, Fe(II) *d-d* and Fe(II)/Fe(III) IVCT, 0.33 AU, E_⊥c)

$$\varepsilon = \frac{Abs}{l*conc} = \frac{0.33}{(0.565\text{ cm})*(0.017\text{ M})} = 35\text{ M}^{-1}\text{cm}^{-1} \quad (11)$$

References

- (1) Ertl, A.; Rossman, G. R.; Hughes, J. M.; Prowatke, S.; Ludwig, T. Mn-Bearing “Oxy-Rossmanite” with Tetrahedrally Coordinated Al and B from Austria: Structure, Chemistry, and Infrared and Optical Spectroscopic Study. *Am. Mineral.* **2005**, *90* (2–3), 481–487.